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POLYMER NANOCOMPOSITES OPEN A NEW DIMENSION FOR PLASTICS AND COMPOSITES

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14. ABSTRACT

For the first time, charging and discharging of traps in the dielectric of state-of-the art RF MEMS capacitive switches were characterized in detail. Densities and time constants of different trap species were extracted under different control voltages. It was found that, while charging and discharging time constants are relatively independent of control voltage, steady-state charge densities increase exponentially with control voltage. A simple charge model was constructed to predict the amount of charge injected into the dielectric and the corresponding shift in actuation voltage. Good agreement was obtained between the model prediction and experimental data.

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Polymer Nanocomposites Open a New Dimension for Plastics and Composites

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Introduction: Nanoengineered Materials

Materials and material development are fundamental to our very culture. We even ascribe major historical periods of our society to materials such as the stone age, bronze age, iron age, steel age (industrial revolution), silicon age and silica age (telecom revolution). This reflects how important materials are to us. We have and always will strive to understand and modify the world around us and the *stuff* of which it is made. The next societal frontiers will be opened not through understanding a particular material, but rather by understanding and optimizing the relative contributions afforded by material combinations.

The nanoscale, and associated excitement surrounding nanoscience and technology (NST), affords unique opportunities to create revolutionary material combinations. These new materials will enable the circumvention of classic material performance trade-offs by accessing new properties and exploiting unique synergism between materials that only occur when the length-scale of morphology and the fundamental physics associated with a property coincide, i.e. on the nanoscale! The confluence of fundamental understanding of materials at this scale and the realization of fabrication and processing techniques that provide simultaneous structural control on the nano-, as well as micro- and macro-, length scales is the core of the exciting area of *nanoengineered materials*. Examples of such material technologies are rapidly increasing, impacting many diverse areas of the commercial and military arena.

One of the ways nanoscience has advanced the state-of-the-art has been to enhance and improve the properties of existing conventional classes of materials. Polymer composites, for example, have been a mainstay of high-performance aircraft for over a quarter century, offering a multitude of desirable (and tailorable) properties, such as high strength and stiffness, and dimensional and thermal stability. With the advent and application of nanotechnology, polymer composites could become even more attractive. As surely as polymer composites changed the face of industry twenty-five years ago, polymer *nanocomposites* will usher in a new era in materials development.
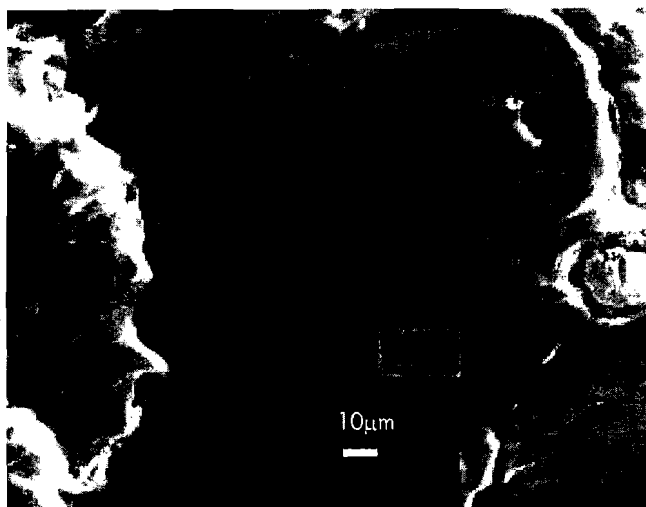

Figure 1. Scanning Electron Micrograph of Conventional Graphite Flake Filler In An Elastomer Matrix. The Inset Shows a Scanning Electron Micrograph of a Collection of ~500 Multi-wall Carbon Nanotubes (MWNT) at the Same Magnification

Polymer Nanocomposites Opportunities

The reinforcement of polymers using fillers, whether inorganic or organic, is common in the production of modern plastics. Polymeric nanocomposites, (PNCs) or the more inclusive term −polymer nanostructured materials, represent a radical alternative to these conventional filled polymers or polymer blends. In contrast to conventional systems where the reinforcement is on the order of microns, PNCs are exemplified by discrete constituents on the order of a few nanometers - ~10,000-times finer than a human hair. The relative size difference between conventional fillers and nanoscale fillers is illustrated in Figure 1.

Uniform dispersion of these nanoscopically-sized filler particles (or *nanoelements*) produces an ultra-large interfacial area per unit volume between the nanoelement and host polymer. For example, interfacial area approaching 700 m^2/cm^3 occur in dispersions of layered silicates in polymers. This is comparable to a football field within a raindrop! These dimensions also imply that the distance between nanoelements is comparable to their size. For a 1nm-thick plate, the distance between plates approaches 10 nm at only 7 vol% of plates. This is a morphology truly dominated by nanoscale features.
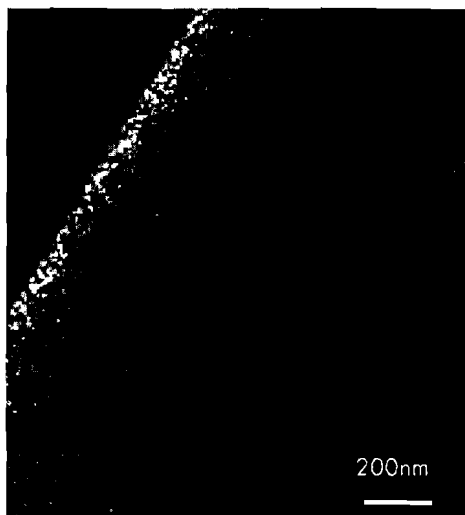
Figure 2. 7nm Ag Nanoparticles in Kapton

Figure 3. Ag-polybenoxazole Fiber

Clay Products and Black-hawk Automotive Plastics announced external automotive body parts made from thermoplastic olefin-layered silicate nanocomposites. A TPO nanocomposite with as little as 2.5% layered silicate is as stiff and much lighter than parts with 10 times the amount of conventional talc filler. The weight savings can reach 20 percent depending on the part and the material that is being replaced by the TPO nanocomposite. On a volume basis, the nanocomposite parts cost about as much as conventional TPOs because less material is needed to manufacture them and no new tooling is required to mold the parts. Overall, the weight advantage could have significant impact on environmental concerns and material recyclibility. For example, it has been reported that widespread use of PLSNs by US vehicle manufacturers could save 1.5 billion liters of gasoline over the life of one year's production of vehicles and reduce related carbon dioxide emissions by more than 10 billion pounds [6].

Considering the plurality of potential nanoelements, polymeric resins and applications, the field of PNCs is immense. Development of multi-component materials, whether microscale or nanoscale, must simultaneously balance four interdependent areas: constituent-selection, fabrication, processing, and performance. For PNCs, this is still in its infancy, and ultimately many perspectives will develop, dictated by the final application of the specific PNC. Two main fabrication methodologies have been developed for PNCs: *in-situ* routes and *exfoliation*. Currently, exfoliation of layered silicates and

This immense internal interfacial area and the nanoscopic dimensions between nanoelements fundamentally differentiate PNCs from traditional composites and filled plastics. These characteristics imply the overall performance of PNCs can not be understood by simple scaling arguments that begin with the behavior of traditional polymer composites. Thus new combinations of properties derived from the nanoscale structure of PNCs provide opportunities to circumvent traditional performance trade-offs associated with conventional reinforced plastics, epitomizing the promise of nanoengineered materials.

From both a commercial and military perspective, the value of PNC technology is not based solely on mechanical enhancements of the neat resin. Rather, its value comes from providing value-added properties not present in the neat resin, without sacrificing its inherent processibility and mechanical properties. Traditionally, blend or composite attempts at 'multifunctional' materials require a trade-off between desired performance, mechanical properties, cost and processibility. The literature is full of examples that suggest PNC technology provides a route around these traditional limitations [1-6].

For example, consider the rapid advance of polymer-layered silicate nanocomposite (PLSN) technology. Efforts within the last 10 years have demonstrated a doubling of the tensile modulus and strength without sacrificing impact resistance for numerous thermoplastic (nylon and thermoplastic olefin {TPO}) and thermoset (urethane, siloxane and epoxy) resins through the addition of as little as 2 vol% layered silicate. Recently, General Motors and partners Basell, Southern
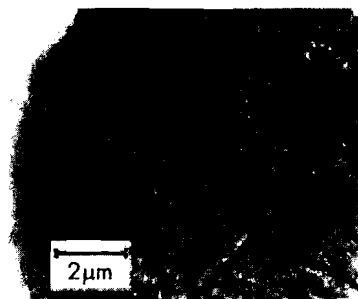

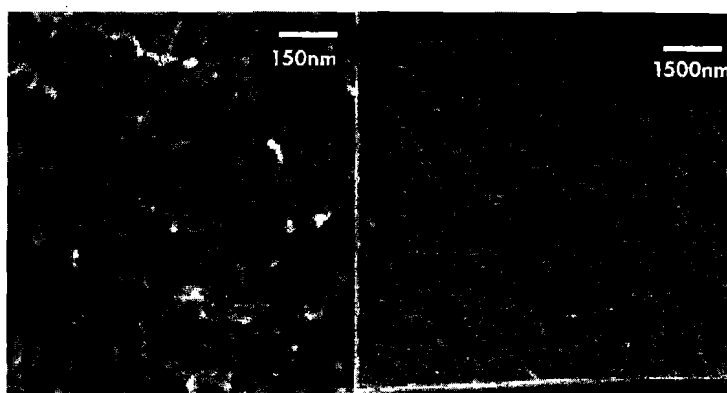**Figure 4. Liquid Crystal Nanodroplets in a Lamella Morphology**

Figure 5. Crystal Structure of 2:1 Layered Silicates (Smectites) [10]

Silicate Layer
0.96 nm

δ −

Exchangeable Cations
(Li+, Na+, K+, Ca+)

Gallery,
Interlayer

δ +

Tetrahedral layer
Octahedral layer
Tetrahedral layer

● O   ● Al, Mg, Fe
● Si   ○ OH

Figure 6. Nylon 6-Layered Silicate Nanocomposite

200 nm

Figure 7. Comparison of Traditional Filled (bottom) vs Nanocomposite (top) Epoxy Optical Properties

carbon nanofibers / nanotubes in commodity and high performance resins are the most heavily investigated PNCs by industrial, government and academic institutions world-wide and will be further discussed below. Some examples of pre-commercial PNCs fabricated via in-situ methodologies are provided in Figures 2, 3 and 4.

In-situ PNCs

In-situ routes to PNCs are based on the creation of the nanoelement within the polymer matrix by chemical means or phase separation. The polymer matrix provides the template within which the nanoelement is formed. An example of this route is the decomposition or chemical reaction of a precursor

introduced to the polymer matrix. Figure 2 depicts 7 nm-Ag nanoparticles formed in the near-surface region of Kapton via a solution infiltration approach that is amenable to microscale pattern formation [7].

Figure 3 depicts a Ag-polybenoxazole nanostructured fiber fabricated via a comparable approach [8]. These fibers are ultra-tough, electrically conductive, ~200-times stronger and ~50% lighter than current aerospace signal wire cores. Another example of the in-situ methodology is chemical or processing perturbation of an initially homogenous polymer system comprised of a blend of two or more chemically discrete constituents to induce a controllable nanoscale phase separation of the constituents.
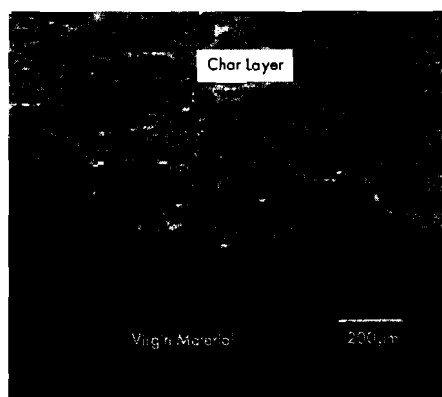
Figure 8a

Figure 8b

**Figure 8. Demonstration
of PLSN Self-passivation
Behavior**

Figure 4 depicts ~70 nm liquid crystal droplets organized with-in a lamella morphology with ~200nm layer spacing formed via holographically-induced liquid crystal phase separation from a photopolymerizable syrup at two magnifications. These struc-tures result in ultrafast (ms) switchable diffractive optics and fil-ters that have military applications. Similar behavior has been demonstrated for patterning nanoparticles in photopolymeriz-able syrups [9]. The interested reader is encouraged to examine the associated references [7-9] and explore related efforts in the literature to disperse, arrange and/or in-situ form quantum dots, oxide nanoparticles, metallic nanoparticles, nanowires, proteins, enzymes, etc. in polymer hosts.

Layered Silicates

Layered silicates (alternatively referred to as 2:1 layered alumi-nosilicates, phyllosilicates, clay minerals and smectites) are the most commonly used inorganic nanoelements in PNC research to-date. Layered silicates possess the same structural character-istics as the well-known minerals talc and mica and are com-

prised of hydrated aluminosilicate [10]. Their crystal structure and habit are summarized in Figure 5.

In the figure, the Van der Waals interlayer (or gallery) con-taining charge-compensating cations (M^+) separates covalently bonded oxide layers, 0.96 nm thick, formed by fusing two sili-ca tetrahedral sheets with an edge-shared octahedral sheet of either alumina or magnesia. The charge per unit cell (generally between 0.5 and 1.3) originates from isomorphous substitution within the silicate layer (e.g. tetrahedral Si^{4+} by Al^{3+} or octahe-dral Al^{3+} by Mg^{2+}). The number of exchangeable interlayer cations is also referred to as the *cation exchange capacity* (CEC). This is generally expressed as milliequivalents/100g, and ranges between 60 and 120 for relevant smectites. Variation in the amount, type and crystallographic origin of the excess layer charge results in a large family of natural (e.g. montmorillonite, hectorite, saponite) and synthetic (e.g. Laponite, fluorohec-torite) layered silicates exhibiting different physical and chemi-cal characteristics, such as layer size, stacking perfection, reac-tivity and Lewis acidity. For example the lateral dimension of the layers range from 20 to 1000 nm.

When exfoliated, an individual sheet is 1 nm thick, with aspect ratios (diameter:thickness) in excess of 100. Conceptually, the process of layered silicate dispersion in poly-mers can be likened to removing, and then arranging, millions of sheets of paper from thousands of tomes on library shelves to uniformly occupy all the free space in the library. The highly anisotropic structure of the silicate layer is critical to provide percolative behavior at low volume fractions, which manifests in numerous physical property increases at small amounts of dispersed layers. Figure 6 depicts the morphology of a Nylon 6 -layered silicate nanocomposite [11]. Dark lines are individual layers of aluminosilicate, 1 nm thick, oriented perpendicular to the sample surface. This structure results in enhanced mechan-ical properties at elevated temperatures, opening new opportu-nities for plastics in the automotive industry [6], as well as reduced water and CO_2 permeability, enabling improved food and beverage packaging [4].

In general, nanoscale dispersion of the layered silicate platelets in resins produces glassy modulus enhancements of one to two times and rubbery modulus increases of 5-20 fold. Related increases in heat distortion temperature and enhanced elevated temperature mechanical properties (strength and mod-ulus) are commonly reported. Additionally, reduced thermal expansivity (CTE), matrix swellability, gaseous permeability and flammability upon 1-5 vol% addition of exfoliated layered silicates will provide new opportunities for various resin sys-tems. An abridged list of polymers investigated with layered sil-icate includes polystyrene, various polyamides (6, 6-6, 11, 12, MDX), polyimides, polypropylene, ethylene vinyl acetate copolymers, poly(styrene-b-butadiene) copolymers (SBS), elas-tomers (PDMS, EPDM, NBR), polyurethanes, poly(ethylene oxide), poly(vinyl alcohol), polyaniline, epoxies, and phenolics. Alexandre et al. [5], Beal and Pinnavaia [2], and Krishnamoorti and Vaia [3] provide summaries of some of the polymers and fabrication routes available in the open literature. The bottom line is that these unique property combinations are observed
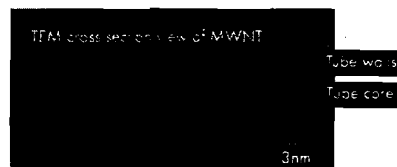
Figure 9a

Figure 9b

Figure 9c

TEM cross section view of MWNT

Tube wall s

Tube core

3nm

100nm
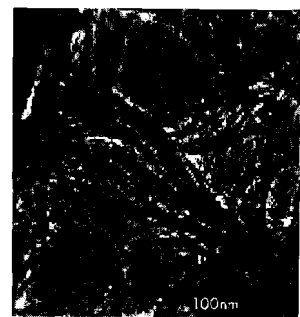
Figure 9d

Tube Axis

Tube wa

Epoxy

**Figure 9. Images of Single-
and Multi-walled Carbon
Nanotubes**

with surprisingly low volume fraction additions of layered sili-
cate (1-5%), thus maintaining polymeric processibility and
reducing weight with respect to micron-scale counterparts
(>20% loading). Note that these comparisons are with regard
to conventional filled polymers and not with regard to contin-
uous fiber reinforced composites. PNCs may provide
enhanced, multi-functional matrix resins, but should not be
construed as a potential replacement for current state-of-the-art
carbon-fiber reinforced composites.

From the military perspective, these enhanced polymer sys-
tems provide opportunities in many venues. In addition to a
general desire for higher-performance, higher use-temperature
resins and thermoplastics, PLSNs provide opportunities to
address material limitations in advanced system concepts.
Combinations of reduced impact resistance, CTE control, sup-
pression of microcracking and increased modulus are currently
being examined for next-generation nanoscale rigid-particulate
reinforced resins for advanced fiber reinforced polymeric com-
posites in unmanned aerial vehicles [12]. Thermal stability and
enhanced fire retardancy through char formation have motivat-
ed investigation of PLSNs as a component to anti-flammabili-
ty additives for aircraft interiors [13]. Superior barrier proper-
ties against gas and vapor transmission have resulted in appli-
cations for food and beverage packaging for military rations
[14] and for barrier liners in storage tanks and fuel lines for
cryogenic fuels in aerospace systems. Also, depending on the
type of polymeric host, PLSNs display interesting ionic con-
ductivity for solid-state electrolytes in batteries [15]. Finally,
along with enhanced scratch resistance and ballistic perform-
ance, the nanoscopic phase dimensions and low volume frac-
tions enable maintenance of optical clarity, critical for scratch-

resistant face shields. Figure 7 compares the optical properties
of traditional filled and nanocomposite epoxy. In the figure the
optical clarity of exfoliated nanoscale morphology (top) is sub-
stantially better than the intercalated, conventional filler mor-
phology at comparable loadings (bottom). Recent efforts have
begun to explore use of layered silicates as ceramic precursors
that will react in-situ with aggressive environments to form a
tough ceramic passivation layer on the polymer surface.
Examples of such self-passivation/self healing during exposure
to a solid-rocket motor exhaust (top) and plasma environments
(bottom) [16] are shown in Figure 8. Combinations of the self-
passivation response with CTE control provide unique alterna-
tives to current materials being examined for inflatable mem-
branes for space antennas and solar collectors. Survivability in
real space environments is currently being examined for PLSNs
and other polymer nanocomposites through an exposure exper-
iment on-board the International Space Station [17].

Carbon Nanotubes

In contrast to the 25+ year investigation of layered silicate dis-
persion in polymers, exploration of carbon nanotubes disper-
sion is relatively new, hindered until recently by the limited
availability of nanotubes. However, nanotube-polymer
nanocomposites are garnishing substantial attention today
because carbon nanotubes offer opportunities to impart unique
electrical and thermal properties to the polymer resin as well as
to enhance mechanical and physical response. Figure 9 briefly
summarizes the structural aspects of carbon nanotubes [18].
Tube diameters can range from 1-100 nm with aspect ratios
(length : diameter) in excess of 100 or 1000! As with the lay-
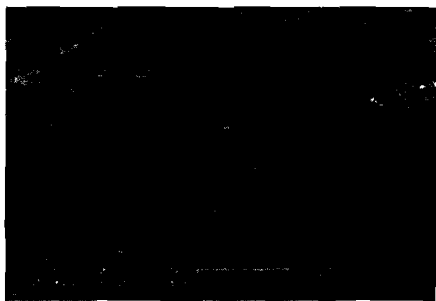ered silicates, the highly anisotropic nature of the tube is criti-

Figure 10. Scanning Electron Micrograph of MWNT Dispersion In Silicone Matrix [20]

cal to provide percolative behavior at low volume fractions, resulting in graphite-like electrical and thermal properties at 1-2 vol% additions.

Overall, carbon nanotubes (i.e. nanoscopically hollow fibers) are generally considered in two categories: single wall nanotubes (SWNT) and multi-wall nanotubes (MWNT). SWNTs are comprised of an individual graphene sheet (Figure 9a). The individual tubes nominally aggregate into 'ropes' consisting of face-center packed individual tubes. Figure 9b shows a transmission electron micrograph (TEM) of a random mat of these SWNT ropes (Figures 9a and 9b courtesy of R. Smalley, cnt.rice.edu/pics.html.) Substantial technological excitement surrounds single-wall carbon nanotubes, based on theoretical prediction and initial experimental verification of incredible mechanical properties (E ~1 TPa [19]) and metal-like electrical conductivity [18] of individual tubes. MWNTs are comprised of nested single-wall tubes (Figure 9c). The external surface of a MWNT is a graphene plane and the individual graphene sheets within the tube interact via van der Waals forces. Alternative gaseous MWNT fabrication routes also produce a bamboo-like structure (Figure 9d) comprised of short segments containing nested tubes with a finite orientation with respect to the overall MWNT axis (courtesy Applied Sciences, Inc.). Terminal strained graphene sheets decorate the surface of these tubes, providing chemical sites for facile surface functionalization and interfacial tailorability.

Challenges associated with the development of low-cost manufacturing approaches, the processibility of raw SWNT products and the maintenance of the SWNT properties during nanotube-polymer fabrication and processing is limiting rapid success of SWNT as polymer nanofillers. Current prices range from $500-$1000 per gram for purified SWNTs. Nonetheless, substantial academic and government investigations are currently addressing these issues.

In contrast, the commercial availability of multiwall nanotubes (MWNT) at $60-$100 per pound is facilitating exciting successes today. Motivated by similar product considerations as discussed for the PLSN systems (provide comparable mechanical properties as achieved with microscale fillers, but at lower

loadings, while maintaining processibility and delivering additional functionality), numerous pre-commercial successes have been reported. For example, MWNTs have been used as direct replacements to carbon-black in paint powders, providing sufficient electrical conductivity at an order of magnitude lower filler loading to enable electrostatic powder coating of automotive parts (e.g. Hyperion Catalysis Int.). The ability to chemically tailor the external surface of the tube while maintaining complete graphene planes within the tube core provides substantial flexibility to independently tailor mechanical, electrical and interfacial properties. A potential drawback to MWNTs relative to SWNTs is decreased mechanical reinforcement because of the weak bonding between the graphene planes within the tube. However, current applications driving nanotube reinforced plastics appear to be motivated more by addition of electrical and thermal properties than by substantial (10-100x) mechanical property increases, and thus MWNTs are expected to make substantial contributions in this arena. Figure 10 shows homogeneously dispersed carbon MWNTs in an elastomer matrix, providing a conductive plastic with elastomeric extensibility in excess of 500% [20].

From the military perspective, tailoring electrical or thermal conductivity of polymer films, fibers or monoliths with very low loadings provides revolutionary opportunities, spanning from electro-magnetic shielding to thermally conductive composites to electrostatic discharge layers to smart fabrics for the future solider. Furthermore, since these nanocomposites can be tailored to be responsive to applied electrical fields, a range of adaptive structures is envisioned. Even more revolutionary is the concept of using the nanoscale percolative network of tubes to controllably remove or transport electrical charge to nanoscopically structured polymer regions between the tubes, providing the foundation for technologies ranging from next-generation flexible photovoltaics to conformal antennas to energy storage devices. The potential impact is pervasive, even greater than that envisioned for PLSNs.

Challenges

Notwithstanding the considerable advances, excitement and promise of exfoliated PNCs, substantial fundamental research is still necessary to provide a basic understanding of these materials to enable full exploitation of their nanoengineering potential. Despite the large number of combinations of matrices and potential reinforcing nanoelements with different chemistry, size, shape and properties, all PNCs share common features with regard to fabrication methodologies, processing, morphology characterization and fundamental physics.

The objective of PNC fabrication via exfoliation methodology is to uniformly disperse and distribute the inorganic filler, initially comprised of aggregates of the nanoparticles, within the polymer. The final PNC structure results from the transformation of the initially microscopic heterogeneous system to a nanoscopically homogenous system. In general, four approaches have been developed to fabricate PNCs via exfoliation - *solution processing, mesophase mediated processing, in-situ polymeriza-*

tion and *melt processing*. Each methodology has advantages with respect to the processing steps necessitated by the desired final form of the PNC (powder, film, paste, fiber, bulk monolith). Substantial research efforts currently endeavor to address the fundamental challenge of providing general guidelines, including thermodynamic, kinetic and rheological considerations for morphology control via these fabrication processes. For example, many potential military opportunities depend on successful incorporation of the nanoelements in thermoset resins. Surface functionalization must be carefully chosen to control polymerization rates and initiation points such that separation of the aggregate of nanoelements occurs before or during polymerization. This is because the extent of cross-linking reactions determines the gel-point of the matrix, and ultimately the extent of exfoliation, hence the final PNC morphology [21]. Additional complications arise from preferential partitioning of the various chemical components in these multicomponent resin systems (reactive oligomer, prepolymer, cross-linker, catalyst, etc.,) to the nanoelement surface modifying reactivities and creating unknown gradients in network topology.

The key to any of these fabrication processes is the engineering of the polymer-nanoparticle interface. Surfactants are commonly used to facilitate this process. These range from small molecules ionically associated with the nanoparticle surface, such as with layered silicates, to chemically bound small molecules or physi-absorbed polymers for nanotubes. These surface modifiers mediate interlayer interactions by effectively lowering the interfacial free energy. Furthermore, they may serve to catalyze interfacial interactions, initiate polymerizations, or serve as anchoring points for the matrix and thereby improve the strength of the interface between the polymer and inorganic filler. However, choice of the optimal modifier to date is at best empirical. Most efforts currently focus on developing interfacial tailoring that achieves dispersion. This is done without regard to providing the necessary thermal stability and desired interfacial response for final form processing, or without a priori determination of the desired interfacial characteristics (e.g. strong, intermediate or weak bonding) to maximize material performance. However, these later considerations are paramount to providing components that have a reliable service life.

Developing an understanding of the characteristics of this interphase region, its dependence on nanoelement surface chemistry, the relative arrangement of constituents, and ultimately its relationship to the PNC properties is a current research frontier in nanocomposites. Equally important is the development of a general understanding of the morphology-property relationships for mechanical, barrier and thermal response of these systems. This necessitates determining the critical length and temporal scale at which the continuum description of a physical process gives way to mesoscopic and atomistic views of these nanoscale systems. This is one of the current challenges for the burgeoning field of computational materials science (see AMPTIAC newsletters Vol. 5, #2 and Vol. 5, #3 for extensive information on the topic of Computational Materials Science).

Summary

Polymer nanocomposites is a rapidly growing area of nano-engineered materials, providing lighter weight alternatives to conventional, filled plastics with additional functionality associated with nanoscale specific, value-added properties. If the promise and excitement surrounding layered silicates and carbon nanotubes are any indication, the future of PNC technology is truly boundless. The opportunities to extend PNC concepts to other nanoelements and polymer hosts are immense, opening the way to provide tailor-made materials that circumvent current limitations and enable future concepts for the DOD and the defense community at large.

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